Low-Energy Termination of Graphene Edges via the Formation of Narrow Nanotubes

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We demonstrate that free graphene sheet edges can curl back on themselves, reconstructing as nanotubes. This results in lower formation energies than any other nonfunctionalized edge structure reported to date in the literature. We determine the critical tube size and formation barrier and compare with density functional simulations of other edge terminations including a new reconstructed Klein edge. Simulated high resolution electron microscopy images show why such rolled edges may be difficult to detect. Rolled zigzag edges serve as metallic conduction channels, separated from the neighboring bulk graphene by a chain of insulating sp^3-carbon atoms, and introduce van Hove singularities into the graphene density of states.

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The atomic structure of graphene and graphene edges is a subject of great interest, in particular, stimulated by new aberration corrected atomic resolution electron microscopy studies [1,2]. Edge structure can define the chemical and electronic properties of graphene ribbons [3], yet there is no consensus about the most stable free edge structure. Unterminated edges, consisting in a line of atoms with dangling bonds, are inherently unstable and subject to chemical functionalization in ambient. However, under vacuum conditions, such as in electron microscope columns, unterminated edges can be observed. Simply cutting through the graphene lattice results in the most studied edge structures: armchair or zigzag, or a combination of the two. The first way that free edges can stabilize themselves is via rehybridization of the carbon atoms. This occurs spontaneously for the armchair edge giving a sequence of double bonds along the edge. The zigzag edge has also been shown to be metastable and undergo a 5-7 reconstruction [4], which has been recently experimentally confirmed [5]. High resolution transmission electron microscopy (HRTEM) suggests that alternative edge structures may also be common, including the theoretically less stable zigzag and Klein edges [2,6–11]. Other reconstructed edges, loosely based on the Haeckelite structures [12], have also been proposed [1]. Besides reconstruction, HRTEM [2,6–11,13,14] has shown that free edges can fold back on themselves, resulting in no longer a graphene monolayer (so-called grafold [15]). The energetic cost of bending the layer is partially compensated by van der Waals interactions in the stacked region.

In this Letter we extend the range of edge types, introducing a third type of stabilized edge whereby edges are rolled back on themselves and rebonded into the graphene sheet. This results in a graphene monolayer with nanotube at the edge site, and eliminates all dangling bonds by sp^3-like rehybridization of the carbon atoms along the rebonding line.

We perform spin polarized density functional calculations under the local density approximation using the AIMPRO code [16]. Graphene edges are modeled using ribbons with width ~50 Å in orthogonal supercells large enough to avoid interaction between neighboring cells. Tubular rolled edges were created symmetrically on both of the two ends of the graphene ribbon. Edge formation energies per unit length (eV/Å) are determined via

$$E_{\text{form}} = \frac{E_{\text{tot}} - n\mu_C}{2L},$$

where E_{tot} is the total internal energy of a system with n carbon atoms, μ_C is the energy of a carbon atom in a perfect graphene sheet, and L is the ribbon edge length. Reaction barriers were calculated using the climbing nudged elastic band method (NEB) [17], with all atoms allowed to move. More details are given in the Supplemental Material [18].

We begin by considering formation energies for zigzag, armchair, 5-7 reconstructed zigzag, Klein [19], and reconstructed Klein edges (Fig. 1 and Supplemental Material [18]). In all cases no out of plane distortion (e.g., edge rippling) was found after relaxation. In agreement with results of Ref. [4], we obtain the armchair and 5-7 reconstructed zigzag edges to be the most energetically stable. The least stable is the Klein edge with unsaturated carbon

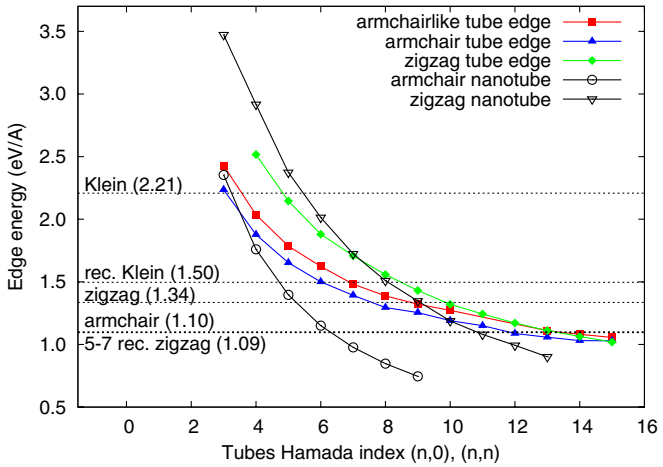

FIG. 1 (color online). Formation energy (eV/Å) for different graphene edges (dashed lines indicated on the figure: Klein, reconstructed Klein, zigzag, armchair, and 5-7 reconstructed zigzag), freestanding zigzag and armchair tubes, armchair-, armchairlike-, and zigzag-tube terminated edges.

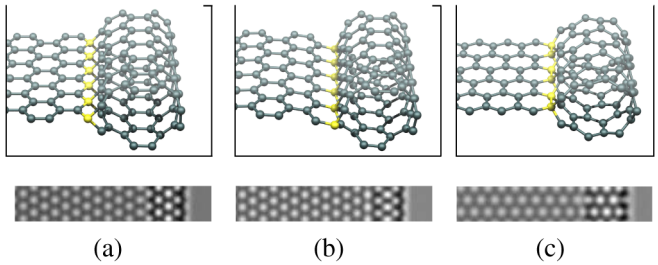

FIG. 2 (color online). Upper panels: Structure of (4,4) armchair (a), (4,4) armchairlike (b), and (8,0) zigzag (c) nanotube-terminated graphene sheet. sp^3-like coordinated carbon atoms are marked in light gray (yellow). Bottom panels: Corresponding simulated HRTEM images.

atoms; however, if symmetry is allowed to break, it spontaneously reconstructs by rebonding in pairs, gaining ~0.7 eV/Å (see Supplemental Material [18]). Segments of the unreconstructed Klein edge were recently observed by annular dark field microscopy [6,20], but the observed Klein edges might have residual hydrogen not detectable by annular dark field microscopy.

A new type of termination leading to the stabilization of the edge can be achieved by taking an unreconstructed free edge, folding it back on itself, and bonding the edge dangling bonds to a line of basal graphene atoms. A rolled zigzag edge can bond into the graphene plane in two configurations: either above what would be zigzag edge atoms or Klein edge atoms. Rolled armchair edges can only bond to equivalent armchair edge atoms. Drawing on nanotube nomenclature we refer to these new edges as armchair-nanotube terminated [Fig. 2(a)], armchairlike-nanotube terminated [Fig. 2(b)], and zigzag-nanotube terminated [Fig. 2(c)], respectively. In all cases the line of carbon atoms bridging the tube and graphene layer adopts an sp^3-like hybridization with average bond lengths (~1.50 Å) and angles (~108°) close to those of diamond. Locally, the structure is similar to the core of the zigzag prismatic dislocation in AA graphite [21]. The sp^3-like bonding allows the tube to localize strain, resulting in a droplet-shaped cross section (Fig. 2).

Figure 1 presents formation energies for different types of free and tube terminated edges as a function of the Hamada index of the tube. For comparison we plot the values for freestanding armchair and zigzag tubes. Consistent with an earlier study [22], freestanding small tubes with diameters below 4 Å [i.e., (3,3) and (5,0) and below] are unstable compared to a flat graphene sheet. This means that it is thermodynamically preferable to split these tubes open, even with unfunctionalized edges. Indeed experimentally these small radii nanotubes have not been observed on their own, but they can exist as inner tubes in large multiwalled nanotubes [23]. We see here, however, that such small nanotubes are more stable when formed on graphene ribbon edges, through localization of the nanotube strain along the sp^3-coordinated tetrahedral bonding line, e.g., a (3,3) armchair tube and all zigzag tubes up to (7,0). Comparing to free zigzag, edges become more stable when rolled in tubes above (8,8). Rolled armchair edges have a lower energy than free edges when forming nanotubes larger than (14,0). For the largest presented tube terminated edges, formation energies are lower than any of the previously proposed free edge configurations.

If we extrapolate to larger diameter tubes we might expect that they collapse due to van der Waals interactions between walls to a dog-bone cross section [24]. However, the droplet cross section induced by the line of sp^3-like carbon atoms naturally induces a "local collapse," and this pinched region extends farther as the tube diameter increases. Thus for large diameters, rolled edges converge to a classical folded edge which then terminates some distance from the actual edge via a line of sp^3-like bonds. We note that in no case is the combination of a free tube and graphene edge more stable than the nanotube-terminated edge [25]; i.e., there will be no thermodynamic driving force for nanotube production from rolled edges.

We next examined the barrier to roll up the edges, determining the barrier between the free zigzag edge and an armchair-nanotube terminated edge as a function of the final tube size. For a (4,4) nanotube-terminated edge, we find a NEB barrier for ribbon rolling of about 2 eV/Å, with a corresponding unrolling barrier of 0.9 eV/Å. For a (8,8) nanotube-terminated edge barriers change to 1.3 eV/Å to roll versus 1.6 eV/Å for derolling. Increasing further the tube diameter gives tube reconstructed edges more stable than free edges, and this induces a barrier height inversion. In particular, for small tubes these barriers are quite high, due to the high curvature that has to be induced. However, these represent maximum barriers, and experimental barriers will likely be much smaller, since

our calculations assume concerted simultaneous bonding or debonding along the entire edge length. Similar to dislocation motion, which proceeds via the propagation of kinks along the dislocation line rather than a concerted single-step motion, rolled edges will presumably roll or unroll initially at a single point which will then propagate along the nanotube length.

Given their low formation energies compared to free zigzag edges, we can ask the question why such tube terminated edges have not yet been reported in the literature. One reason is that these edges require long-range order, whereas other edge structures can vary over the order of single unit cells. Thus we may expect such edges to be more common in well-defined periodic ribbon edges such as after splitting of large multiwalled nanotubes. We note also that freestanding graphene can be obtained through wet etching after epitaxial growth on metal substrate [26]. We expect that during the etching process rolled edges might appear as in analogous synthesis mechanisms used for the production of inorganic nanotubular materials [27]. Furthermore, rolled edges could be difficult to discriminate by transmission electron microscopy. Simulated HRTEM images (Fig. 2) are very similar to those of freestanding edges, the primary difference being minor variations in the image contrast. Additionally, these edges may display characteristic nanotube modes detectable using spatially resolved resonant Raman.

We next examine the effect of rolled edges on the electronic properties of the graphene. We present in Fig. 3 the electronic density of states for the (8,8) and (8,0) tube terminated edges. These show an interesting combination of the graphene and nanotube behavior. In spite of different electronic character of freestanding (8,8) and (8,0) tubes, i.e., metallic and semiconducting, in both cases the composite system has a nonzero density of states at the Fermi level. For a zigzag-tube termination the background density of states around the Fermi level rises smoothly, reflecting the graphene density of states, overlaid on which there is a series of van Hove singularities characteristic of a nanotube. For the armchair-tube terminated edge, i.e., a rolled zigzag graphene edge, there is a sharp peak at the Fermi level similar to that seen for flat unterminated zigzag edges [3,4]. Such Fermi level peaks can lead to magnetic instability, and indeed our spin unrestricted calculations show a ferromagnetic configuration to be the lowest energy state (slightly lowering of the edge energy of the system by only 0.02 eV/Å), although this must be treated with caution given the use of the local density approximation.

The peak consists of two degenerate states which can be seen in the associated band structure [Fig. 4(a)] as involving a mixing of several bands. Plotting these states at the Γ and X point [Fig. 4(b)] shows that the Fermi level spike is localized mainly on the row of graphene atoms next to the sp^3-carbon atoms, mirroring the edge state seen in flat zigzag terminated graphene [3], whereas at the X point the highest occupied state comes from dispersive edge states located in the nanotube segment along the junction. This convergence of three zigzag edges at the line of sp^3-bonded carbon atoms suggests possible interesting magnetic behavior under an applied field.

We note that the zigzag metallic edge state is preserved in this configuration, and unlike the unterminated simple zigzag edge it will also be partially protected from environmental attack, since all neighboring atoms are fully coordinated. Notably we might expect it to be stable in air. These states also suggest intriguing transport behavior, with possible conduction channels both along the edge of the graphene and in the edge states in the nanotube segment.

In summary, we have shown that by rolling an unterminated graphene edge it is possible to create

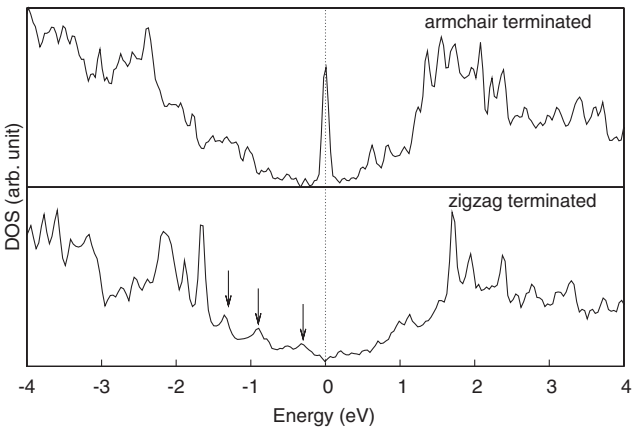

FIG. 3. Calculated density of states (DOS) for (a) (8,8) armchair- and (b) (8,0) zigzag-nanotube terminated graphene edge. The van Hove singularities are marked by arrows.

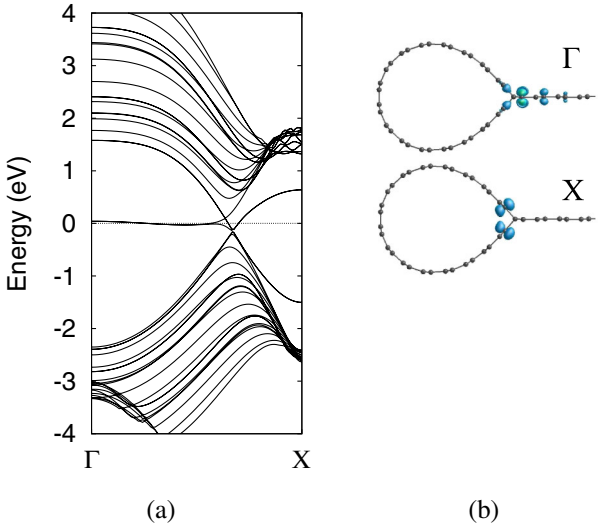

FIG. 4 (color online). (a) Band structure for (8,8) armchair-nanotube terminated edges and (b) distribution of highest occupied state at the Γ point and X point.

nanotube-terminated edges where the sheet edge rebonds back into the graphene plane. We determine the critical tube size and formation barriers and compare with density functional simulations of other edge terminations including a new reconstructed Klein edge. We find that the proposed tube terminated edges are more stable than any other nonfunctionalized edge structure, due to the replacement of dangling bonds with sp^3-like hybridized carbon atoms. Rolled zigzag edges serve as metallic conduction channels, separated from the neighboring bulk graphene by a chain of insulating sp^3-carbon atoms, and introduce van Hove singularities into the graphene density of states. They may provide a way to stabilize and protect from chemical attack the disperse Fermi level state seen along metallic zigzag edges. Similar edge rolling effects might also appear in other layered materials [28] such as boron nitride monolayers where orbital rehybridization can occur.

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